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Gemini Surfactant-Modified Activated Carbon for Remediation of Hexavalent Chromium from Water

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Abstract: Gemini surfactants, with double hydrophilic and hydrophobic groups, offer potentially orders of magnitude greater surface activity compared to similar single unit molecules. A cationic Gemini surfactant (Propyl didodecyldimethylammonium Bromide, PDDDAB) and a conventional cationic surfactant (Dodecyltrimethylammonium Bromide, DTAB) were used to pre-treat and generate activated carbon. The removal efficiency of the surfactant-modified activated carbon through adsorption of chromium(VI) was investigated under controlled laboratory conditions. Fourier-transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM) were used to investigate the surface changes of surfactant-modified activated carbon. The effect of important parameters such as adsorbent dosage, pH, ionic strength and contact time were also investigated. The chromium(VI) was adsorbed more significantly on the Gemini surfactant-modified activated carbon than on the conventional surfactant-modified activated carbon. The correlation coefficients show the data best fit the Freundlich model, which confirms the monolayer adsorption of chromium(VI) onto Gemini surfactant-modified activated carbon. From this assessment, the surfactant-modified (especially Gemini surfactant-modified) activated carbon in this study showed promise for practical applications to treat water pollution.

Keywords: Gemini surfactant; modification; chromium(VI); adsorption; activated carbon

1. Introduction

Because of its ecotoxicity, and common occurrence in industrially affected environments, chromium pollution has gained a high profile [1]. The hexavalent oxidation state of chromium is more toxic than other forms in water and can cause serious illness or even death [2,3]. According to the Chinese law for wastewater discharge, the maximum levels permitted for total chromium are 0.5 mg/L and for hexavalent chromium are 0.2 mg/L. At present, the methods of controlling chromium pollution include chemical precipitation, ion exchange, reduction, adsorption, extraction, membrane filtration and biosorption treatment [4–7]. Approaches using adsorption are considered to have potentially the best treatment effect [8]; modified activated carbon can enhance the adsorption performance of activated carbon, and potentially provides a high efficiency and low cost adsorbent for treating chromium(VI) pollution [9,10].

Activated carbon adsorption is non-selective, and the adsorption process is susceptible to interference, especially metal cations, and many studies show that surfactant-modified activated carbon can enhance the adsorption capacity of metal ions [11]. Ewecharoen [12] used sodium polyacrylate to graft to activated carbon, and obtained good performance for nickel removal. Peñas-Sanjuán [13] used polyalkylamine as the activated carbon surfactant, it has excellent removal performance for Pd (II). Sun [11] used amine-crosslinked copolymer to modify activated carbon, which was more efficient than

the original activated carbon in the treatment of chromium wastewater, and the influencing factors and mechanism of adsorption were explored. A modified activated carbon treated by ethylenediamine provided better Cr (VI) removal under visible light [14]. Treatment with green synthetic nano-zinc oxide also produced activated carbon, which performed strongly in treating chromium in solution [15]. A summary of recent studies on the capability of activated carbon to remove heavy metals is provided in Table 1.

Different from those traditional surfactants (such as DTAB), which contain one hydrophobic chain and one hydrophilic group in their “amphiphilic” structure, the Gemini surfactant molecules (such as PDDAB) contain two hydrophilic groups, two hydrophobic chains and a rigid spacer. Because of this molecule structure, Gemini surfactant may offer orders of magnitude greater surface activity compared to similar single unit molecule. We report here the design and evaluation of the efficiency and mechanism of removal of heavy metals by using Gemini surfactant-modified activated carbon.

Table 1. Examples of treatments for activated carbon in applications to remove heavy metals from the aqueous phase.

Treatment Step	Effect	Reference
Nitric acid, ammonium persulfate and hydrogen peroxide in the solution with gaseous oxygen at 350 °C	The adsorption of Cr(III) increased but Cr(VI) decreased on oxidation	[16]
Using (NH ₄) ₂ S ₂ O ₈ in 1 M H ₂ SO ₄ to oxidize carbon materials	The adsorption of Zn(II) increased but surface area and carbon porosity decreased after oxidation under static conditions	[17]
Making acidic oxygen functional groups into activated carbon by HNO ₃ oxidation	The adsorption of cadmium increased after oxidized and decreased significantly after heat treatment to progressively eliminate the oxygen functional groups of various thermal stability	[18]
Heat treatment (1200 K) in nitrogen, air oxidation (693 K), and nitric acid treatment of activated carbons	Have a much higher Hg ⁰ adsorption capacity (925 mg/g)	[19]
Using carbon (1.5 mm) and heating from ambient temperature to 900 °C in SO ₂	The adsorption of Cd ²⁺ was 70.3%. The maximum adsorption (88.3%) of Pb(II) with initial lead concentration of 50 mg/L	[20]
Modified with 1.0 M citric acid and 1.0 M NaOH	The adsorption capacity was increased to 14.92 mg/g, which was 140% higher than the unmodified carbon	[21,22]
Heat treatment under the atmosphere of NH ₃ after pre-oxidation with HNO ₃	The higher adsorption rate and capacity toward Cu(II) was obtained	[23]
Modified with iron salt solution	The optimum removal of As(III), As(V), Fe, and Mn were 93%, 98%, 100%, and 41%, respectively	[24]
Modified with iron hydro (oxide) nanoparticles	Their maximum arsenic adsorption capacity varied from 370 ug/g to 1250 ug/g	[25]

2. Materials and Methods

2.1. Materials and Instrument

The reagents used in this study were: powdered activated carbon (AC, analytical grade, Tianjin Kemiou Chemical Reagent Co., Ltd., Tianjin, China), acetone (chromatography pure, Tianjin Kemiou Chemical Reagent Co., Ltd., Tianjin, China), potassium dichromate (analytical grade, Tianjin Kemiou Chemical Reagent Co., Ltd., Tianjin, China), sulfuric acid (excellent grade pure, Tianjin Kemiou Chemical Reagent Co., Ltd., Tianjin, China), hydrochloric acid (excellent grade pure, Tianjin Kemiou

Chemical Reagent Co., Ltd., Tianjin, China), phosphoric acid (excellent Pure, Tianjin Kemiou Chemical Reagent Co., Ltd., Tianjin, China), sodium hydroxide (excellent grade pure, Tianjin Kemiou Chemical Reagent Co., Ltd., Tianjin, China), Dodecyltrimethylammonium Bromide (DTAB, molecular formula: $\text{CH}_3(\text{CH}_2)_{11}(\text{CH}_3)_3\text{NBr}$, purity: analytically pure, Tianjin Kemiou Chemical Reagent Co., Ltd., Tianjin, China), Propyl didodecyldimethylammonium Bromide (PDDDAB, molecular formula: $[\text{CH}_3(\text{CH}_2)_{11}(\text{CH}_3)_2\text{NBr}]_2(\text{CH}_2)_3$, 50% pure, Henan Titanning Chemical Technology Co., Ltd., Baoshun, China).

The instruments used in this study were: Ultraviolet and visible spectrophotometer (WFZ UV-2000, Unico (Shanghai) Instrument Co., Ltd., Shanghai, China), Scanning electron microscopy (SEM, JSM-6380LV, JEOL Ltd., Akishima, Japan), Fourier transform infrared spectrometer (FTIR, Nicolet 6700, Thermo Electron Corporation, Waltham, MA, America), Electronic analytical balance (FA2004, Hengping (Shanghai) Instrument Co., Ltd., Shanghai, China), Electric drying oven with forced convection (GZX-9070 MBE, INESA, Shanghai, China), Magnetic stirrer (GSP-80-04, Analyse instrument (Jiangsu), Jiangsu, China), Electronic thermostat electric sets (DZTW, INESA, Shanghai, China) etc.

2.2. Preparation of Surfactant-Modified AC

Samples of powdered activated carbon (10 g) were weighed into the 100 mL-Erlenmeyer flask, with 1 g modifier and 25 mL deionized water, then placed on magnetic stirrer with low-speed stirring of the reaction mixture for 24 h. Subsequently filtered and the filter-cake dried to constant weight at 70 °C, rushed, weighed and stored.

2.3. Adsorption Experiment

The standard stock solution of 100 mg/L Cr(VI) was prepared by using solid potassium dichromate. The 20 mg/L Cr(VI) solution sample for the experiment was obtained by dilution and for the kinetic experimental work was diluted as needed, and adjusted to target pH with HCl and sodium NaOH (1:1 v/v). A 50 mL sample of Cr(VI) solution was placed in the reaction bottle, with an aliquot of modified activated carbon, and subject to reaction conditions over an appropriate period of time.

2.4. Measurement and Analysis

The concentration of Cr(VI) was determined by Absorption Spectroscopy (UV-vis). The process of determination was that 2 mL reaction solution was filtered through a 0.45 µm filter, and diluted to 50 mL. A 0.5 mL portion of sulfuric acid and phosphoric acid (1:1 v/v) was added and 2 mL of indicator, and shaken well for 2–10 min. The concentration of hexavalent chromium in the solution was determined from absorbance at (540 nm) after reaction. The maximum measurement was 1 mg/L and the minimum measurement was 0.2 µg/L. The structural characteristics of surfactant-modified AC were observed by SEM, and the change of the active bond was observed by FTIR.

The isothermal adsorption models of Langmuir and Freundlich were used to describe the isothermal adsorption behavior of adsorbents; the kinetic process is described by quasi-first-order adsorption kinetics model and quasi-second-order adsorption kinetic model.

3. Results and Discussion

3.1. Surface Characteristics and Functional Group Analysis

The AC, DTAB-AC, PDDDAB-AC SEM images are shown in Figure 1. Compared with those figures, the surface of the activated carbon was changed obviously under the influence of the modifier. Figure 1a is the unmodified activated carbon, which has a smooth and regular surface and dense structure without a gap. Under the modification of DTAB and PDDDAB (Figure 1b,c), the activated carbon exhibits a rough surface and a large number of cavities.

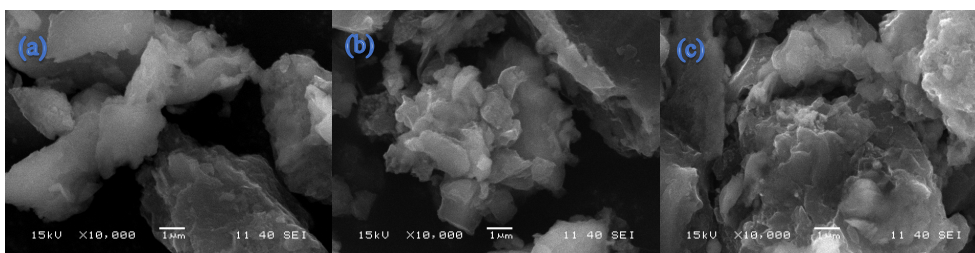


Figure 1. SEM images of AC (a); DTAB-AC (b); PDDAB-AC (c).

Infrared spectrum of activated carbon is shown in Figure 2. We know that the -CH_3 stretching vibration generates a peak at 3423 cm^{-1} , the peak at 1617 cm^{-1} can be attributed to $\text{C}=\text{C}$ from activated carbon skeleton, the peak at 1465 cm^{-1} can be attributed to $\text{-CH}_2\text{-}$, at 1186 cm^{-1} can be attributed to $\text{-CH}_2\text{-}$, and at 3018 cm^{-1} can be attributed to methyl quaternary ammonium salt. After modification, the absorption peak of the functional groups is clearly stronger. Combined with the SEM map and the structure of DTAB and PDDAB (Figure 3). The modification process increases the density of functional groups, which can provide more coordination positions and higher adsorption of Cr (VI) ions.

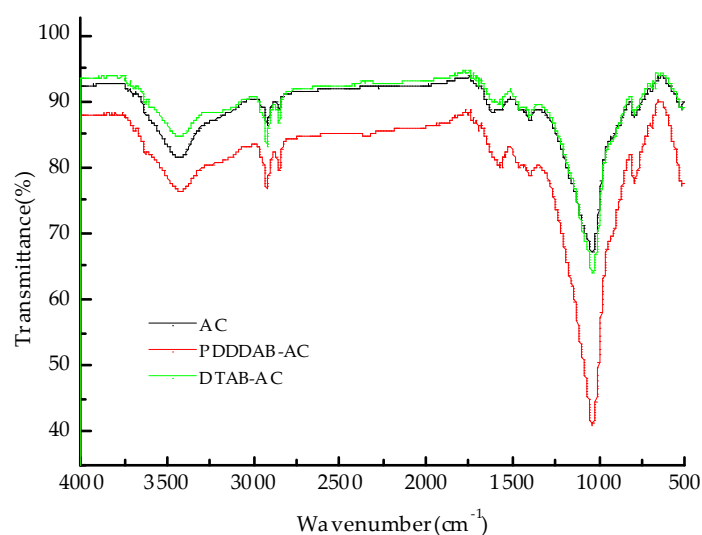


Figure 2. Infrared spectroscopy of Activated carbon and surfactant-modified materials.

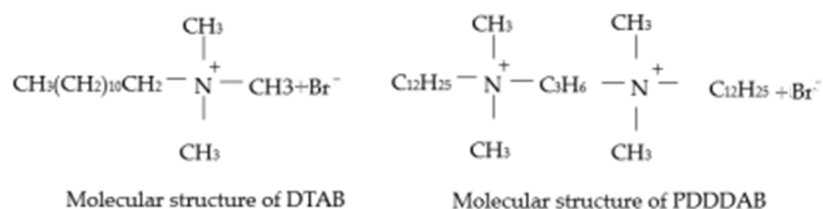


Figure 3. The molecular structure of DTAB and PDDAB.

3.2. Adsorption Effect of Cr (VI) at Different Modifier Dosage

Activated carbon, modified by 7 different concentrations (0.1%, 0.2%, 0.5%, 1%, 2%, 5% and 10%) of PDDAB/DTAB respectively, were weighed with precision of 0.5 g into 7 reaction bottles, with a 50 mL sample of solution. The concentration of chromium in the solution was determined after shaking for 7 h on the shaker at the room temperature. Figure 4 shows the removal rate changes with the modifier concentration. As the concentration of the modifier increases, the removal rate of

Cr(VI) in the raw water increases. Due to the hydrophobic interaction between activated carbon and modifier [26], activated carbon has a strong ability to fix PDDAB and DTAB. Studies have shown that anion exchange and electrostatic adsorption are the main adsorption mechanisms for cationic surfactant-modified activated carbon [27]. The reaction can be described by the following reaction equation: when the concentration of modifier and the removal rate of chromium by modified activated carbon are higher, the removal rate of activated carbon to modifier is higher. When the carrying capacity reaches the maximum, the removal is in a steady state. In the experiment, when the maximum load was selected, the concentration of the modifier was 10%.



where AC and M^- is activated carbon and chromate ion respectively. PDDAB is a Propane diamine didodecyl dimethyl ammonium bromide, Br^- is bromide ion and DTAB is Dodecyl trimethyl ammonium Bromide, M_{Cr^-} is chromate ion.

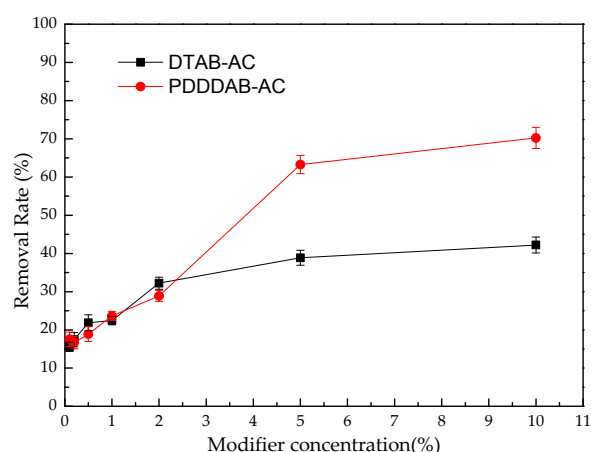


Figure 4. Effect of modifier concentration on Cr(VI) removal.

3.3. Adsorption Effect of Cr (VI) at Different Adsorbent Dosage

Samples of modified activated carbon 0.04g, 0.06g, 0.1g, 0.2g, 0.5g and 1g were weighed precisely into 6 reaction bottles, with a 50 mL sample of solution. The concentration of chromium in the solution was determined after shaking for 4 h on the shaker at the room temperature. According to Figure 5, with the increase of the adsorbent concentration, the removal rate of chromium increases (Figure 5a) and the adsorption capacity of chromium decreases from the initial chromium concentration (Figure 5b). As the concentration increases it reaches a concentration where the adsorption tends to be balanced, and PDDAB-AC chromium removal rate is much higher than the DTAB-AC. The effect is due to that with the increasing adsorbent dosage, the total number of adsorption sites increased, which allowed the removal rate to increase. When the volume and mass concentration of Cr (VI) solution remain constant, increasing the adsorbent concentration will increase the amount of adsorbent in the unsaturated state [28], so that the total adsorption capacity appears to decrease. It can be seen from Figure 5a that PDDAB-AC provides higher capacity for the adsorption of Cr (VI), and consequently has better adsorption effect.

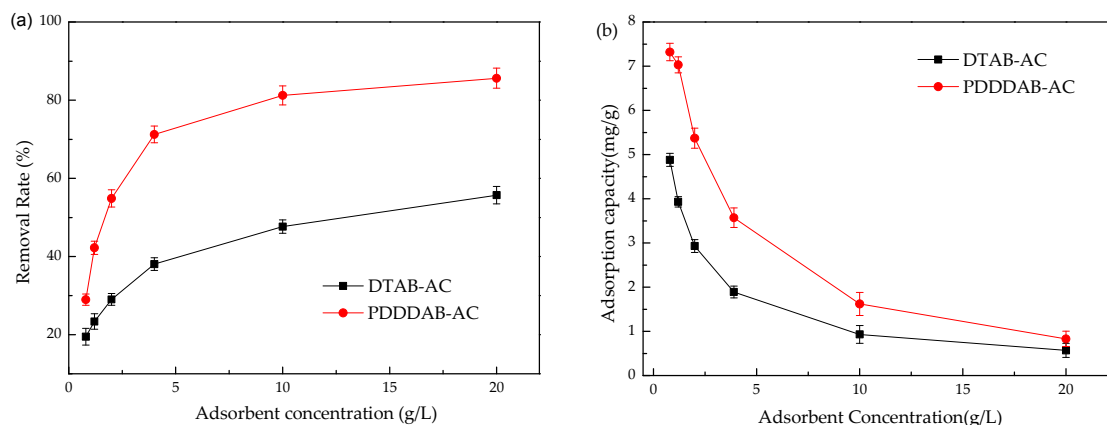


Figure 5. The removal rate (a) and the adsorption capacity (b) of chromium with adsorbent concentration.

3.4. Adsorption Effect of Cr (VI) at Different pH

A series of 0.5 g samples of modified activated carbon were weighed into 6 reaction bottles with 50 mL sample solution and the solution pH value was adjusted to 4, 5, 6, 7, 8, 9, and 10, using hydrochloric acid and sodium hydroxide (1:1 *v/v*). The concentration of chromium in the solution was determined after shaking for 4 h on the shaker at the room temperature. As shown in Figure 6, the removal rate for chromium decreases as the pH increases and this phenomenon is not obvious under the acidic conditions, but significant under alkaline conditions. The PDDAB-AC has less of an effect than DTAB-AC and adapts to pH change. It has its highest removal rate at pH of 4–6 in this study.

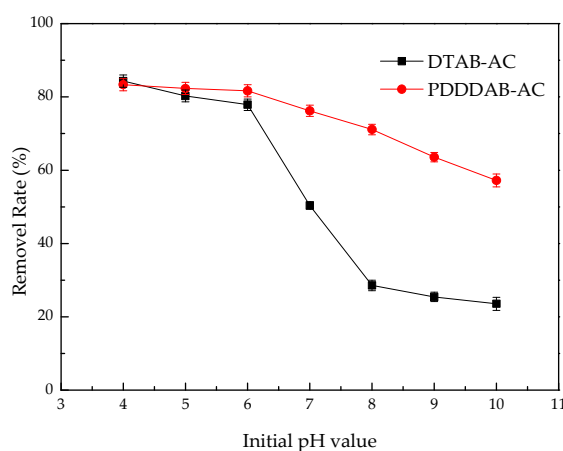
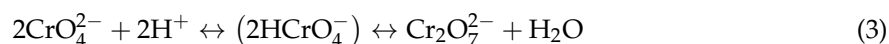


Figure 6. Effect of initial pH value on Cr(VI) removal.

Some studies have previously shown that the removal of chromium worsens as the pH increases [29]. The appearance of this phenomenon is related to the nature of the activated carbon and the form in which Cr is present in the solution [30]. The main form exists of hexavalent chromium in water environment include CrO_4^{2-} , HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$. The stability is susceptible to the pH value of the solution, the redox substances and other conditions, it also can be interconverted under certain conditions [31].



when the pH value of the solution is less than 7, Cr (VI) anions are mainly present in the form of HCrO_4^- , a HCrO_4^- anion is adsorbed by ion exchange with Br^- on the modified activated carbon. At the same time, the functional groups such as hydroxyl groups, carboxyl groups and carbonyl groups on the surface of activated carbon can react with hydrogen ions to form cations, so that the

surface of the activated carbon carries a positive charge and the electrostatic force increased, with consequently enhanced adsorption capacity of activated carbon for Cr (VI). As the pH value increases, when the pH is greater than 6, the hexavalent chromium anion is progressively transformed its existing form from HCrO_4^- to CrO_4^{2-} . The ion exchange mechanism is based on equimolar charge relationship. Each mole of CrO_4^{2-} requires 2 moles of charge, the adsorption capacity of Cr (VI) decreases when the adsorption point is constant. Under the conditions that the pH value is more than 7, the carboxyl groups on the surface of activated carbon can react with OH^- and form carboxylate ion, so that the surface of the activated carbon carries negative charge. The electrostatic attraction between modified activated carbon and the same negatively charged Cr (VI) anion is weakened and is not conducive to adsorption. However, when the pH increases, the concentration of OH^- ion increases, and the competitive adsorption of Cr (VI) anions increases, which also affects the adsorption of Cr (VI). Some studies have identified that there is a conversion between hexavalent chromium and trivalent chromium in solution due to the presence of redox reaction [11], which affects this process.

3.5. Adsorption Effect of Cr (VI) at Different Ionic Strength

Samples of 0.5 g modified activated carbon were weighed into 6 reaction bottles with 50 mL solution sample and concentration of NaCl in solution was 0 mmol/L, 5 mmol/L, 10 mmol/L, 20 mmol/L, 30 mmol/L, 40 mmol/L, 50 mmol/L, 60 mmol/L. The concentration of chromium in the solution was determined after shaking for 4 h on the shaker at the room temperature. According to Figure 7, the effect of ionic strength on the adsorption of chromium by two kinds of modified activated carbon is significant, the removal rate decreases significantly with the increase of ionic strength in the reaction solution, the removal rate of DTAB-AC and PDDDAB-AC were below 10% when the NaCl concentration was greater than 40–60 mmol/L, the presence of a large amount of Cl^- ions in the solution produces a strong competitive adsorption with chromate ions and inhibits the adsorption of chromium [32]. This conclusion is in accordance with the statement that the adsorption of hexavalent chromium anions by modified activated carbon is based on the main mechanism of ion exchange and electrostatic adsorption. The ionic reaction formula is shown in Equations (1) and (2). Studies have shown that NaCl makes hexavalent chromium ions display a “salting-in” effect [13], so that the distribution of adsorbate in the solution increased. The presence of NaCl may agglomerate the adsorbent, resulting in a decrease in the number of adsorption points [33].

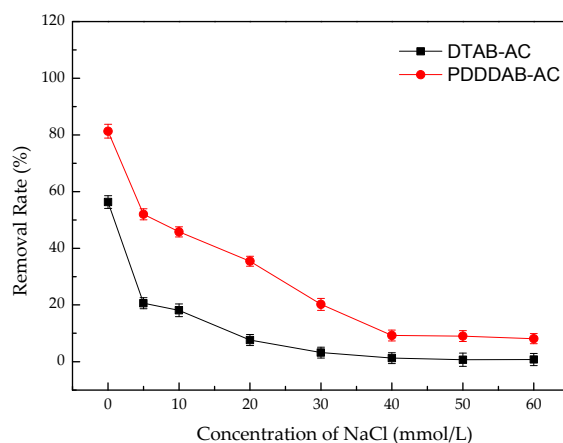


Figure 7. Effects of NaCl on Cr(VI) removal.

3.6. Adsorption Isotherms

Modified activated carbon was weighed with precision of 0.5 g into 2 sets of reactors, with 50 mL solution sample at pH 4. The concentration of Cr(VI) in the solution was determined after shaking on the shaker at the room temperature.

Langmuir and Freundlich isothermal adsorption models can be used to describe the adsorbent isothermal adsorption behavior to adsorbate. Langmuir [34] (Equation (4)), Freundlich [35] (Equation (5)) isothermal expression is described as follows:

$$\frac{1}{q_e} = \frac{1}{Q} + \frac{1}{QB} \frac{1}{C_e} \quad (4)$$

where: q_e : the saturated adsorption capacity of the unit adsorbent at equilibrium (mg/g); Q : single-layer saturated adsorption capacity of adsorbent (mg/g); C_e : concentration at equilibrium (mg/L); B : Constant associated with temperature or enthalpy change.

$$\ln q_e = \ln K + \frac{1}{n} \ln C_e \quad (5)$$

where: both K and n are Freundlich constants at a certain temperature, K generally decreases with increasing temperature, $1/n$ is generally between 0 and 1.

In this experiment, two adsorption tests were fitted using the linear form of Langmuir adsorption isothermal formula and Freundlich adsorption isothermal formula respectively. The results of the fitting curve are shown in Figures 8 and 9; the fitting degree and the adsorption isotherm equation are listed in Table 2.

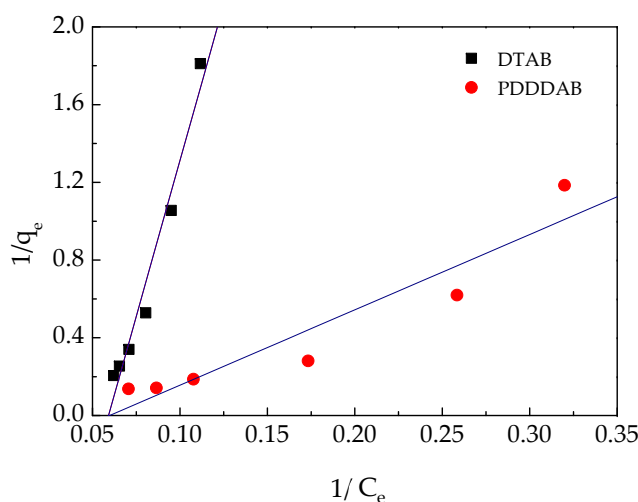


Figure 8. Langmuir adsorption isotherms of Cr(VI) onto PDDDAB and DTAB.

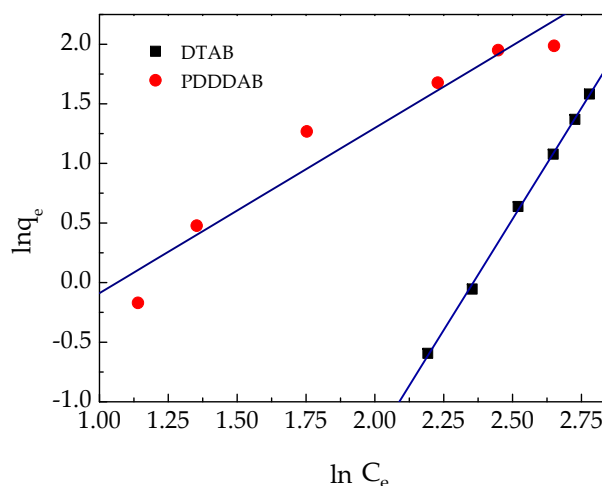


Figure 9. Freundlich adsorption isotherms of Cr(VI) onto PDDDAB and DTAB.

Table 2. Isotherm equations and R^2 of Cr(VI) onto PDDDAB and DTAB.

	Langmuir Model	Freundlich Model
PDDDAB-AC	$\frac{1}{q_e} = 3.876 \frac{1}{C_e} - 0.2312$ $R^2 = 0.8955$	$\ln q_e = 1.3863 \ln C_e - 1.4749$ $R^2 = 0.9396$
DTAB-AC	$\frac{1}{q_e} = 32.102 \frac{1}{C_e} - 1.8984$ $R^2 = 0.9667$	$\ln q_e = 3.7272 \ln C_e - 8.7844$ $R^2 = 0.9991$

From Table 2, due to having high correlation coefficient and R^2 values, the results show that Langmuir and Freundlich isotherm model can correctly describe the adsorption data obtained for Cr(VI) onto both PDDDAB-AC and DTAB-AC. The Langmuir isotherm model suggests that the homogenous surface and the adsorption follow physisorption of monolayer adsorption patterns [36]. The better fit of Freundlich model to adsorption Cr(VI) onto both surfactant-modified activated carbons reveals that the adsorption takes place in the heterogeneous surface and interaction among adsorbed molecules can occur and multilayer adsorption is also possible [36]. Furthermore, the dimensionless constant of separation factor (R_L), which is given in Equation 6, is used to express the fundamental characteristics of the Langmuir isotherm [37].

$$R_L = \frac{1}{1 + bC_0} \quad (6)$$

where C_0 represent the initial concentration of adsorbate (mg/L), b represents Langmuir constants. R_L can take values between 1 and 0. The value of R_L indicates the situation of the isotherm to linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$) [37]. In this study, the value of R_L was found to be between 0 and 1 ($R_{L,PDDDAB-AC} = 0.456$, $R_{L,DTAB-AC} = 0.458$) suggesting that the adsorption of Cr(VI) onto both two surfactant-modified activated carbons is favorable process.

3.7. Adsorption Kinetics

The kinetics of metal ion sorption processes in a batch system is also necessary for determining the type of processes that govern the mechanism of sorption. In this study, the applicability of the pseudo-first-order model (Equation (7)) and pseudo-second-order model (Equation (8)) have been tested for the sorption of Cr(VI) onto modified activated carbons [38]. The best-fit model was selected based on the linear regression correlation coefficient, R^2 values.

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (7)$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \quad (8)$$

where: q_e : unit adsorption of chromium by modified activated carbon at equilibrium time (mg/g); q_t : unit adsorption of chromium by modified activated carbon at time t (mg/g); k_1 is the constant of quasi-first-order model (min^{-1}); k_2 is the constant of quasi-second-order model ($\text{g}/(\text{mg} \cdot \text{min})$).

The kinetic experiments were carried out with 0.5 g DTAB-AC/PDDDAB-AC and 50 mL sample solution at pH 4. The concentration of chromium in the solution was determined repeatedly by sampling the reaction solution after shaking the shaker at room temperature over a 7 h period. The relationship between the adsorption time T and the chromium removal rate was plotted as Figure 10. From this figure, it was observed that DTAB-AC adsorption of chromium in the reaction achieved the maximum removal rate of 70% within 1 min, PDDDAB-AC adsorption of chromium achieved the maximum removal rate of 92% in about 30–60 min. Thereafter, the removal rate was found to be slightly decreased, which may be attributed to physical desorption of Cr(VI) from activated carbon. Finally, the curve of removal rate slowly tends to a smooth line. The final PDDDAB-AC removal rate falls from 92% to about 80%, DTAB-AC adsorption chromium removal rate falls from

70% to 60%. The rapid increase in removal at the initial period may be due to an increased number of vacant sites available at the initial stage, thus there exist increased concentration gradients between adsorbate in solution and adsorbate in the adsorbent surface. This increase in concentration gradients tends to allow rapid increase of Cr(VI) removal at the initial stages [39]. Although DTAB-AC achieves equilibrium in a slightly shorter time than PDDDAB-AC, PDDDAB-AC is more efficient in removal than DTAB-AC, and the equilibrium time of both adsorption reactions was about 4 h.

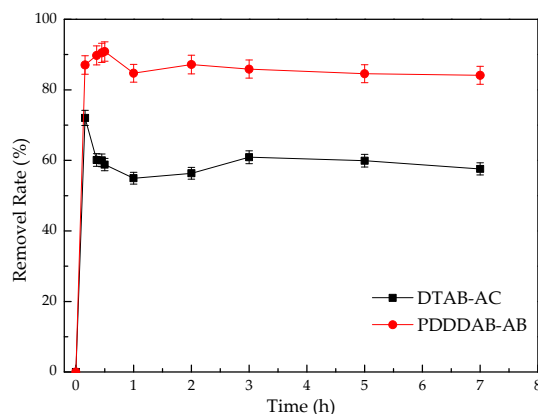


Figure 10. Adsorption kinetics for Cr(VI) onto DTAB-AC and PDDDAB-AC.

Figure 11 shows the pseudo-first-order kinetics model for Cr(VI) onto DTAB-AC and PDDDAB-AC. Figure 12 shows the pseudo-second-order kinetics model for Cr(VI) onto PDDDAB-AC and DTAB-AC, and kinetic modeling equations and those parameters are shown in Table 3.

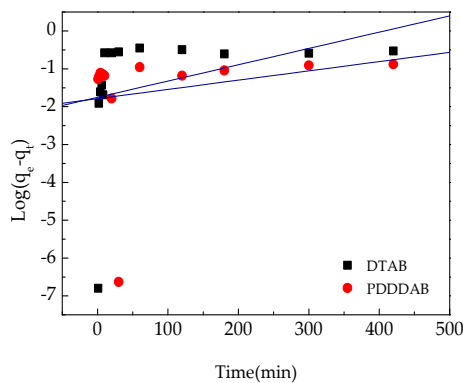


Figure 11. Pseudo-first-order kinetics for Cr(VI) onto PDDDAB-AC and DTAB-AC.

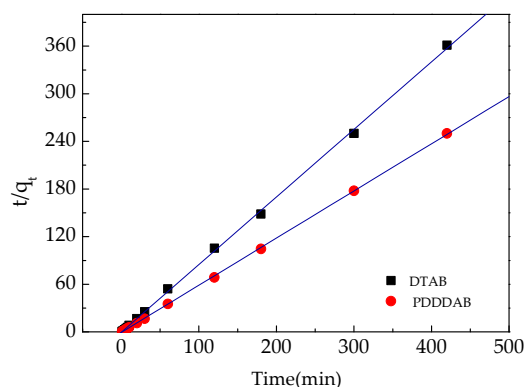


Figure 12. Pseudo-second-order kinetics for Cr(VI) onto PDDDAB-AC and DTAB-AC.

Table 3. Parameters of two kinetic models for Cr(VI) onto PDDDAB-AC and DTAB-AC.

	Pseudo-First-Order Model	Pseudo-Second-Order Model
DTAB-AC	$\log(0.1733 - q_t) = 0.0043t - 1.7529$ $R^2 = 0.1125$	$\frac{t}{q_t} = 0.8514t - 0.2742$ $R^2 = 0.9994$
PDDDAB-AC	$\log(0.1672 - q_t) = 0.0024t - 1.7888$ $R^2 = 0.0454$	$\frac{t}{q_t} = 0.5941t - 0.5915$ $R^2 = 0.9999$

From Table 3, it was observed that, for the uptake of Cr(VI) by both DTAB-AC and PDDDAB-AC, the R^2 values for pseudo-second-order were found to be higher than the R^2 values for pseudo-first-order. This pseudo-second-order kinetics is presumed to proceed via chemisorption, which may involve valence forces through the sharing or exchange of electrons between the surfactant-modified activated carbons and the Cr(VI) ion as covalent forces and ion exchange [40].

4. Conclusion

The removal of Cr(VI) by PDDDAB-AC adsorbent is higher than that of DTAB-AC, the adsorption capacity is larger and the adsorption performance is more superior and more stable. The adsorption properties of two kinds of activated carbon are greatly affected by the ionic strength of solution, and the removal rate decreases as it increases. The removal of chromium in PDDDAB-AC and DTAB-AC decreased with the increase of pH value in the range of pH = 4 ~10, and the removal rate reaches the highest when pH is about 4–6. In this study, it could be concluded that PDDDAB-AC is better than DTAB-AC for Cr(VI) removal.

After about 30–60 min, PDDDAB-AC adsorbent reached a maximum removal of 92%, and the removal rate was 80% at equilibrium, which was significantly higher than that of DTAB-AC and the maximum removal rate was 70% and the removal rate was 60% at equilibrium. It is clear that the uptake of Cr(VI) by PDDDAB-AC is more efficient than those by DTAB-AC.

The comparison of different isotherm models indicated that the Langmuir and Freundlich isotherm models can correctly describe the adsorption data obtained for Cr(VI) onto both PDDDAB-AC and DTAB-AC. The better fit of Freundlich model to adsorption Cr(VI) onto both surfactant-modified activated carbons reveals that the adsorption takes place in the heterogeneous surface and interaction among adsorbed molecules can occur and multilayer adsorption is also possible. Moreover, the adsorption process is favorable. After the kinetic adsorption data were fitted with different kinetic models, a pseudo-second-order kinetic model can better describe the kinetics of two adsorption processes, which indicates that the main adsorption reaction is chemical adsorption.

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